DRAFT OF SLIDES (03/05/91)

STATISTICAL ANALYSIS OF DIOXIN AND FURAN MEASUREMENTS IN ENVIRONMENTAL SAMPLES FROM THE PULP AND PAPER INDUSTRY

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COOPERATIVE STUDY BETWEEN EPA AND PAPER INDUSTRY

All U.S. mills that bleach wood pulps with chlorine or chlorine derivatives (104 Mill Study)

Other studies show that chlorine bleaching is a source of dioxin and furan

Data collected included 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in:

- Effluent (treated or untreated wastewater)
- Sludge (semi-solid residue from treatment system)
- Pulp (fibers after conversion from wood chips)

Data collected in mid to late 1988

Industry managed the program

CONCLUSIONS

For effluent, sludge, and pulp separately:

1. Detected values appear to be lognormally distributed

2. Log-regression methods were appropriate in modeling non-detect measurements

3. Target detection levels are achievable

4. Analytical variability is relatively low

5. Variability due to combined field sampling and analytical error is relatively low

CONCLUSIONS (continued)

For combined outputs of effluent, sludge, and pulp:

6. Greater chlorine use tends to increase TCDD and TCDF discharges

7. Increased chlorine dioxide substitution tends to decrease TCDD and TCDF discharges

RESPONSIBILITIES OF THE NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT (NCASI)

Managed program for industry

Provided guidance to mills on sampling methods

Developed the laboratory analysis method (GC/MS)

Submitted samples to labs

Reviewed lab results

Forwarded results to EPA

6.5

DIFFERENCES BETWEEN NCASI AND EPA LAB ANALYSIS METHODS

NCASI Method 551

EPA Method 1613

Both high resolution GC/MS methods

NCASI 551 limited to 2,3,7,8-TCDD/TCDF

EPA 1613 designed for all 17 2,3,7,8-substituted PCDD/PCDFs

DATA

Each mill provided one sample of effluent, sludge, and pulp

400 samples of effluent, sludge, and pulp
5-day composite samples

80 additional samples for QA/QC

Process information corresponding to sampling dates

QA/QC information (recoveries and ion ratios)

TWO LABS PERFORMED ANALYSES

Wright State University

pulp (80%)

Enseco-California Analytical Laboratories

effluent (89%)

sludge (81%)

PRESENTATION'S EMPHASIS

Effluent

TCDD

Kraft mills

REASONS FOR FOCUSING ON EFFLUENT

Conclusions are similar for sludge and pulp

Confounding factors in sludge and pulp

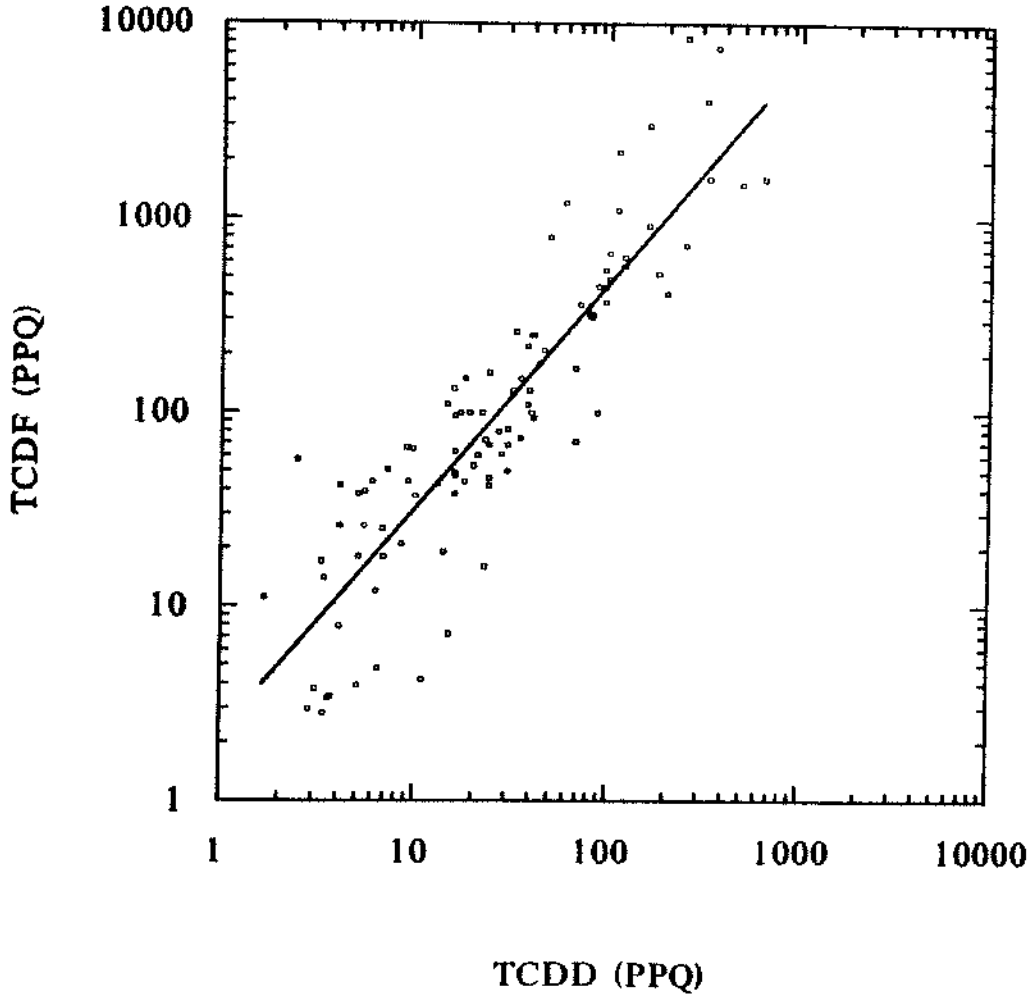
Sludge samples hard to physically obtain

Pulp collected earlier in the process than effluent and sludge

Pulp sampled before drying process

TCDD VS. TCDF: EFFLUENT SAMPLES

KRAFT MILLS



$R^2 = .79$

REASONS FOR FOCUSING ON KRAFT MILLS

Processes are different

Sulfite mills tend to produce less TCDD and TCDF

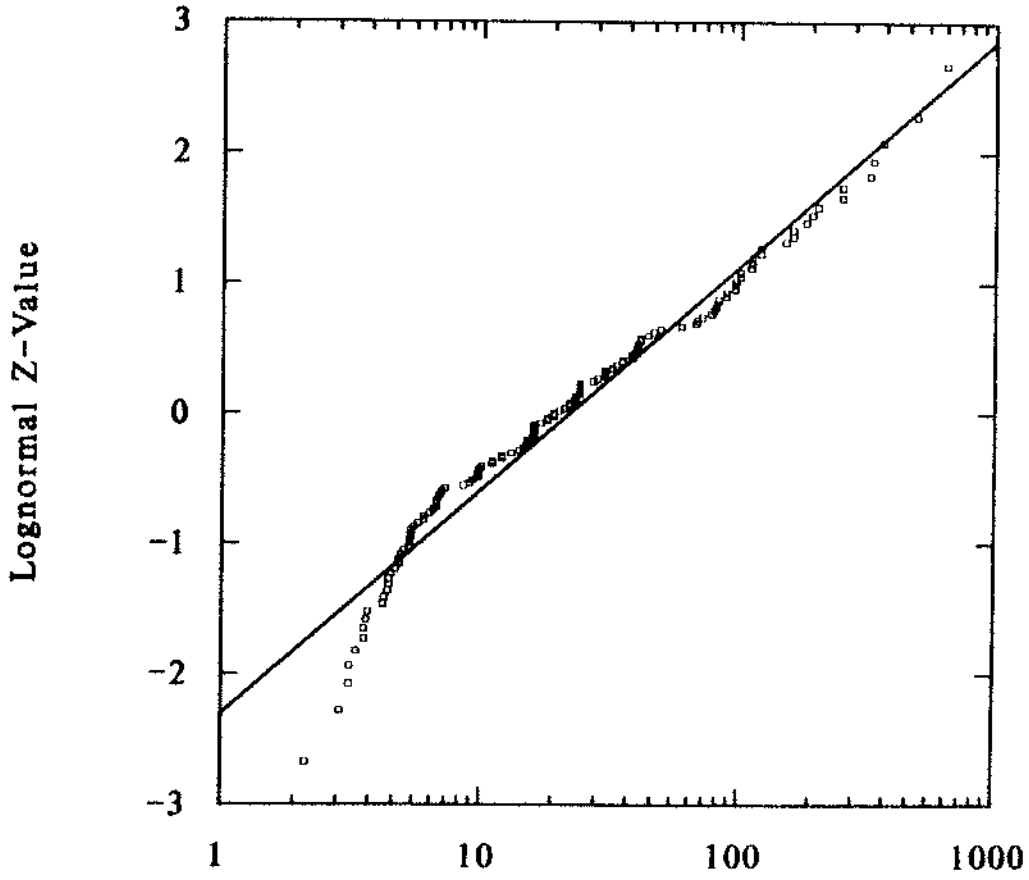
Different types of wastewater treatment

Difficulties with lab analysis of sulfite samples

FIGURE 3-24

EFFLUENT TCDD

NDs ESTIMATED USING DETECTED VALUES ONLY



TREATMENT OF NON-DETECT VALUES

Sensitivity analyses: all methods about the same

Log-regression method best

28% of TCDD samples non-detect in effluent at kraft mills

All mills had detected concentrations of TCDD or TCDF in effluent, sludge, or pulp

TARGET DETECTION LEVEL

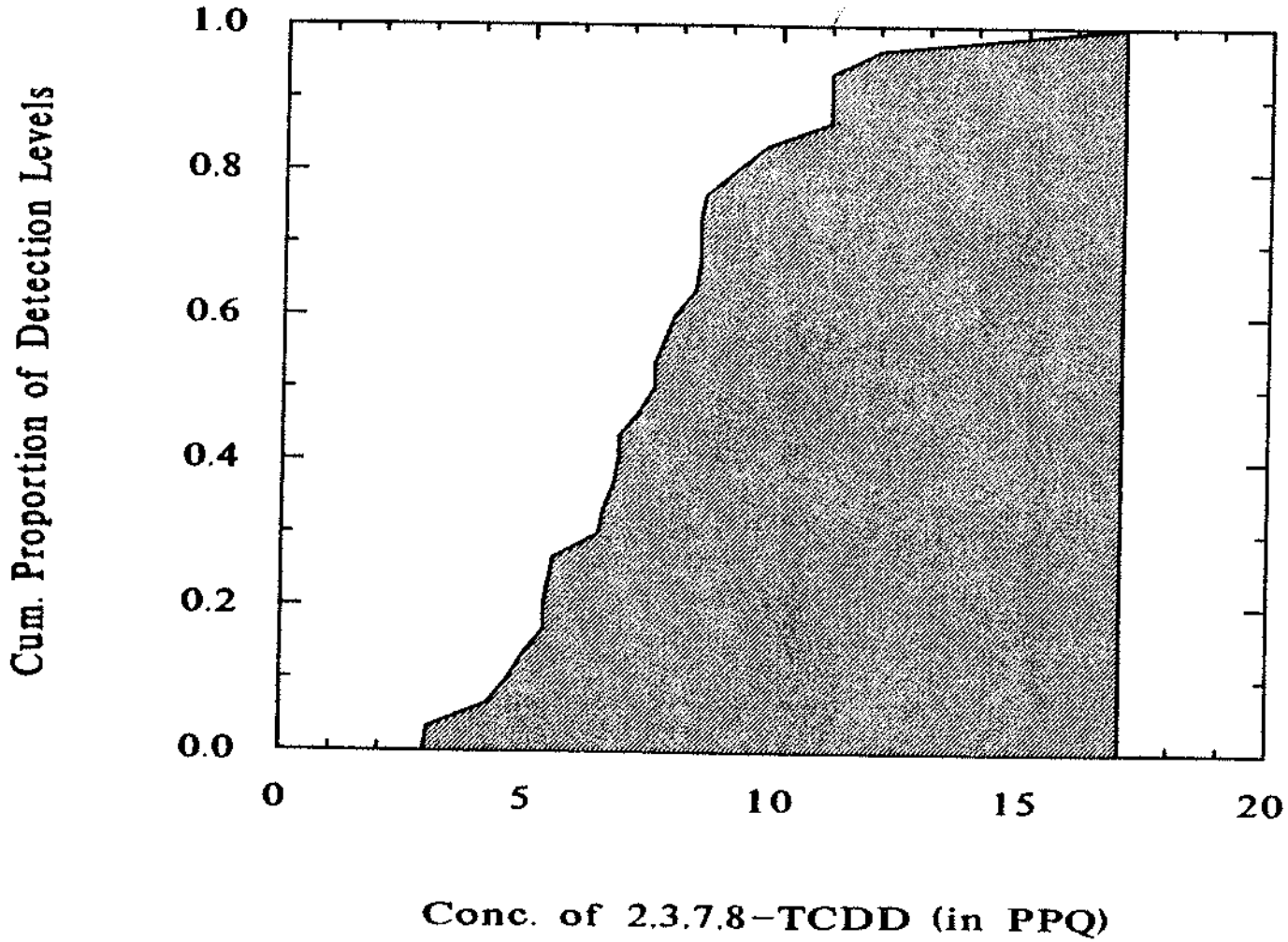
10 ppq for effluent

DETECTION LEVELS FOR NON-DETECT TCDD SAMPLES IN EFFLUENT

Number 30

	Concentration (ppq)
Minimum	3.0
Maximum	17.0
Mean	7.7
Standard Dev.	2.8
Median	7.5

EFFLUENT TCDD DETECTION LEVELS
SAMPLE CUMULATIVE DISTRIBUTION GRAPH



ANALYSIS OF DUPLICATE SAMPLES

	# Samples	# Mills
Effluent	107	84
Duplicates	34	15
Laboratory	15	6
Field	19	9

2 - 3 duplicates from each mill having duplicates

Not all mills provided duplicate samples

ESTIMATES PROVIDED BY ANALYSIS OF DUPLICATE SAMPLES:

Analytical variability

from laboratory duplicate samples

Combined variability due to field sampling and analytical error

from field duplicate samples

ESTIMATES NEEDED FOR:

Impact on averaging duplicates

Response to industry claims of high analytical variability

THE DATA DID NOT SUPPORT AN ANALYSIS OF:

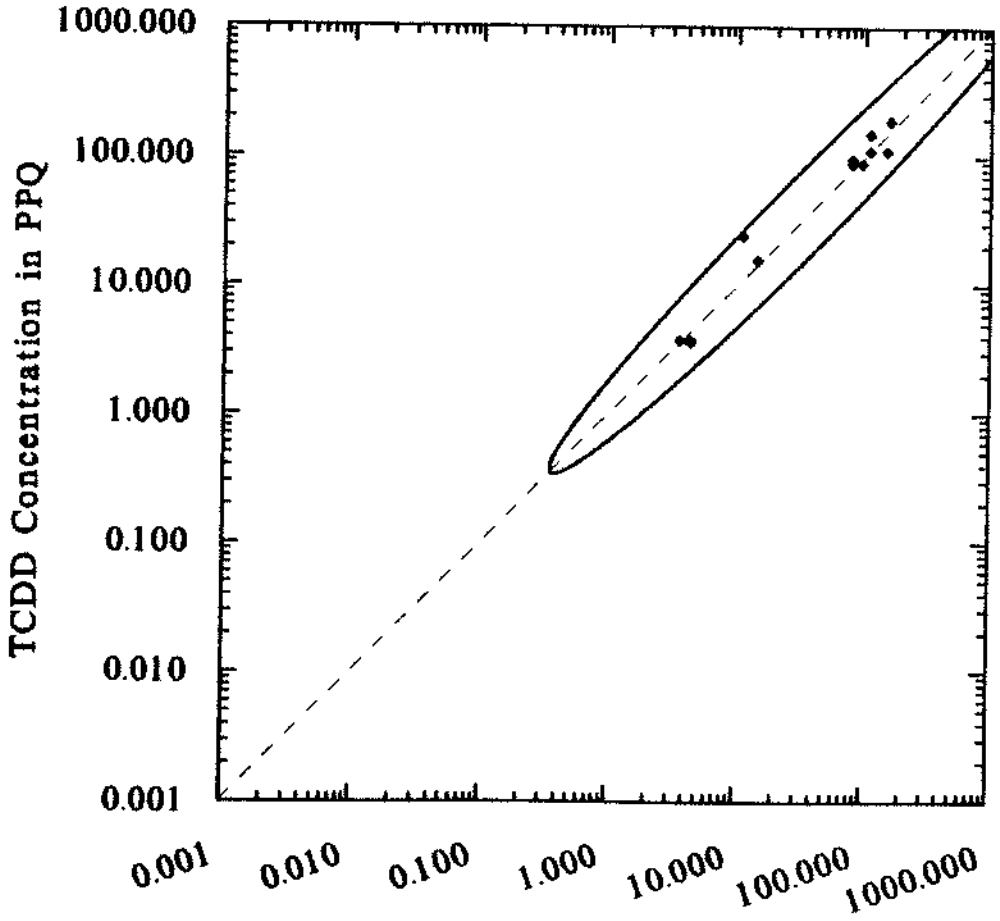
Inter-lab variability

Separate estimate of field sampling variability

TCDD: EFFLUENT LAB DUPLICATES

NON DETECTS = LOG REGRESSION ESTIMATES

KRAFT MILLS ONLY

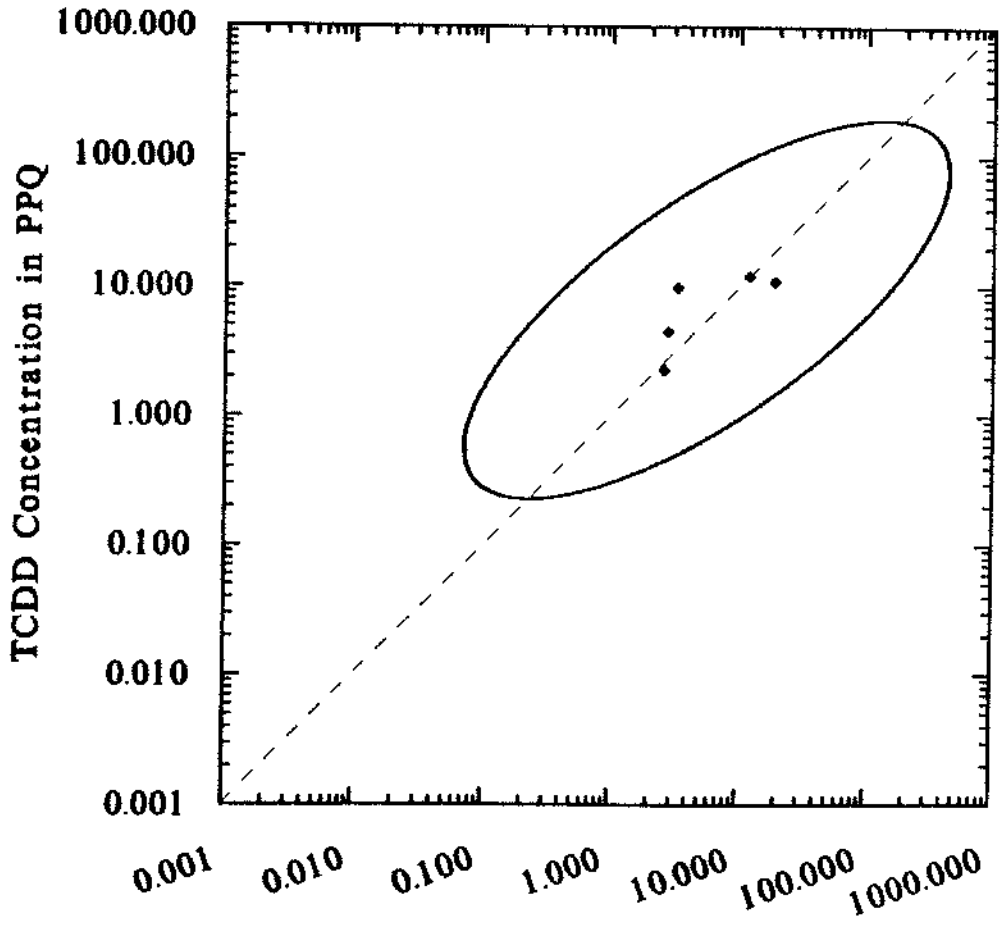


$r = .98$

TCDD: EFFLUENT LAB DUPLICATES

NON DETECTS = LOG REGRESSION ESTIMATES

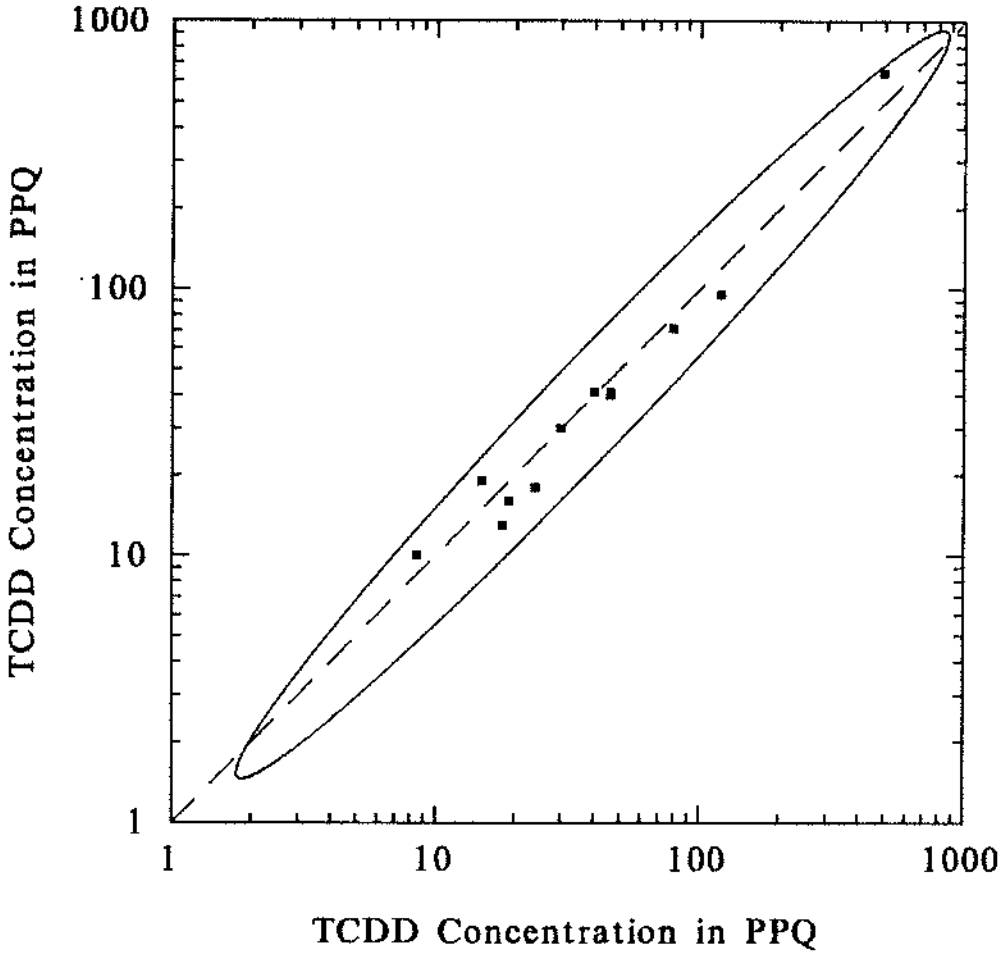
SULFITE MILLS ONLY



r² = .73

TCDD EFFLUENT FIELD DUPLICATES

NON-DETECTS = LOG REGRESSION ESTIMATES
KRAFT MILLS ONLY



r = .99

ANOVA RESULTS FOR EFFLUENT DUPLICATE SAMPLES FROM KRAFT MILLS

	N	SS1	SS1%	SS2	SS2%
LAB DUPLICATES					
Log_{10}(TCDD)	15	5.572	98.60	0.079	1.40
FIELD DUPLICATES					
Log_{10}(TCDD)	19	4.754	99.20	0.038	0.80

SS1 = Between duplicate set sum of squares

SS2 = Within duplicate set sum of squares

CONCLUSIONS FROM ANALYSIS OF DUPLICATES

1. The duplicates could be averaged

2. Relatively low analytical variability

3. Relatively low variability due to field sampling and analytical error

4. Need to look elsewhere for variability

   (e.g., processes or plant management)

OTHER FACTORS INFLUENCING TCDD OUTPUT

Evaluated on basis of combined output from effluent, sludge, and pulp

Combined output adjusted for amount of pulp production by each mill

None of results are strong

Results tend to support industry working hypotheses

THREE FACTORS PRESENTED:

Chlorine usage

Chlorine dioxide substitution

Wood type used to produce the pulp

CHLORINE (Cl_2)

Used in bleaching to whiten pulp

Other studies show TCDD and TCDF produced mostly in chlorination stage

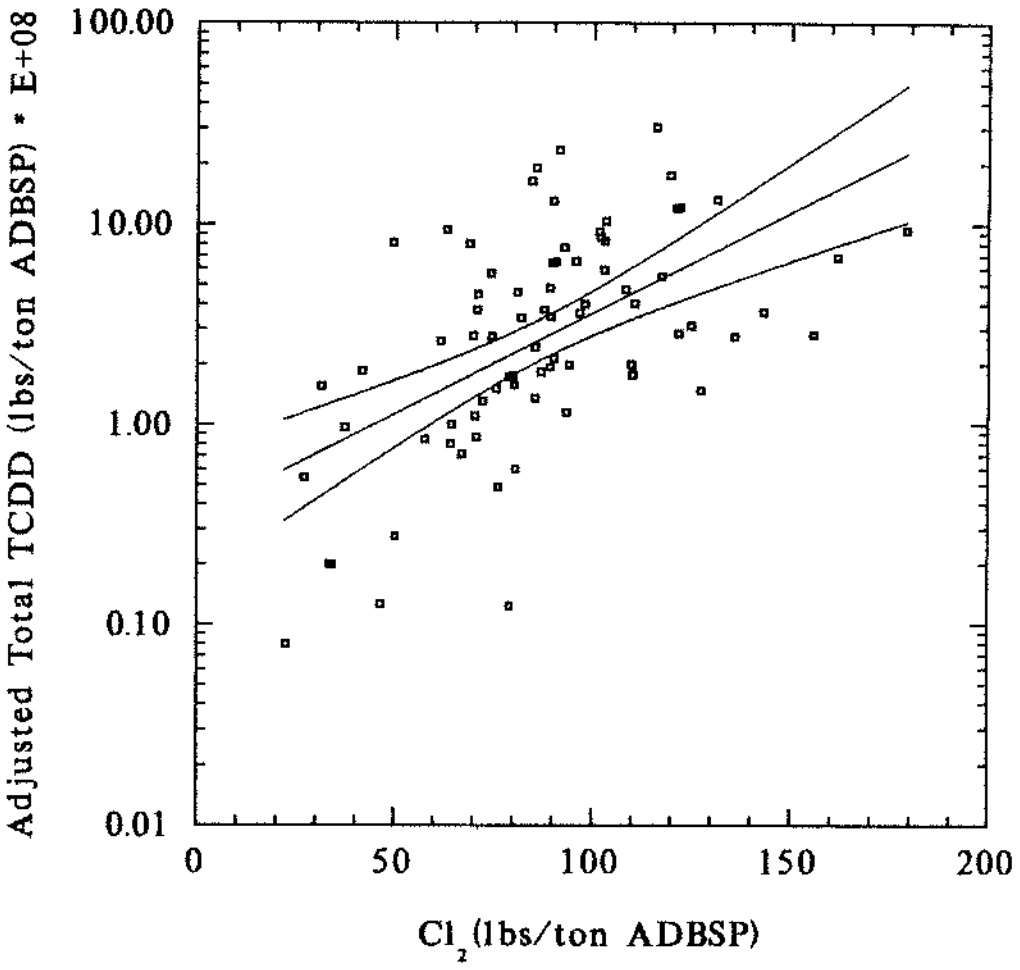
Weak positive relationship between chlorine use and TCDD

30% of variability in data

Problem with over-chlorination

Cl_2 vs. ADJUSTED TOTAL TCDD

NON-DETECTS = LOG REGRESSION ESTIMATES
KRAFT MILLS ONLY



$R^2 = .322$

$\log_{10}(\text{total TCDD}) = -.449 + .010 * Cl_2$

CHLORINE DIOXIDE (ClO_2) SUBSTITUTION

Substituted for chlorine in bleaching process

Used to improve effluent quality

and reduce TCDD and TCDF

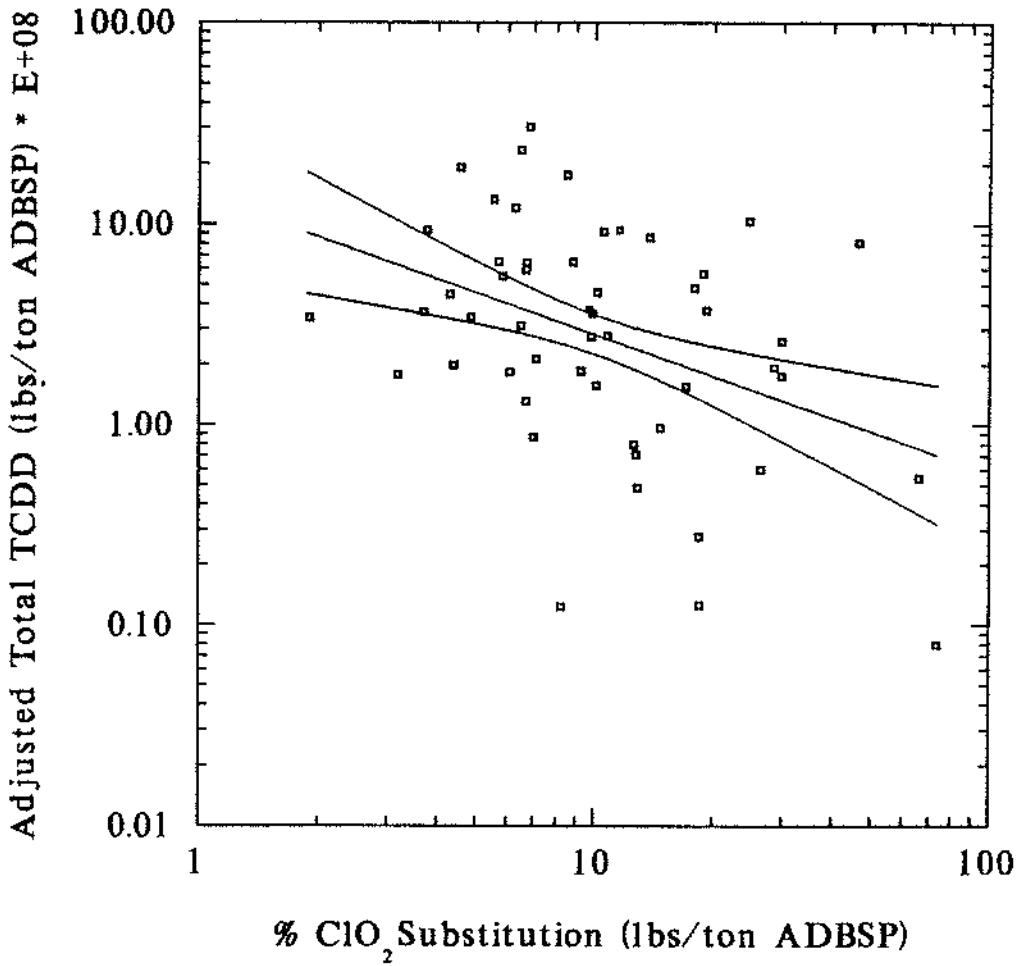
Very few mills substituted more than 30%

Not all mills substituted

Accounts for 16% of variation in data

% ClO_2 vs. ADJUSTED TOTAL TCDD

NON-DETECTS = LOG REGRESSION ESTIMATES
KRAFT MILLS ONLY



$R^2 = 16\%$

$\log_{10}(\text{total TCDD}) = 1.145 - 0.693 * \%ClO_2\ \text{sub}$

CONFOUNDING FACTORS BETWEEN Cl_2 and ClO_2

1. Order chemicals added

2. Adding chemicals in stages

   decreases TCDD and TCDF

3. Competition between two chemicals

   increases TCDD and TCDF

WOOD TYPES

Softwood (e.g., pine, spruce)

Hardwood (e.g., oak, maple)

More chlorine applied to softwood

Analysis found more TCDD and TCDF with softwood

WHAT'S NEXT?

Development of water pollution control regulations

Industry is changing to reduce TCDD and TCDF

EPA is sampling 16 - 19 mills

Long-term sampling planned at four mills

Detailed questionnaire mailed to all facilities

- collects self-monitoring data and process information
- preliminary analysis this fall

Regulation: limits for TCDD and TCDF